



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/GB89/00245 <b>(22) International Filing Date:</b> 10 March 1989 (10.03.89) <b>(31) Priority Application Number:</b> 8806605 <b>(32) Priority Date:</b> 19 March 1988 (19.03.88) <b>(33) Priority Country:</b> GB  <b>(71)(72) Applicant and Inventor:</b> ROBINSON, Eric [GB/GB]; 146 Moss Road, Lambeg, Lisburn, Antrim BT27 4LF (GB).  <b>(81) Designated States:</b> AT (European patent), BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), NO, SE (European patent), US.		<b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> COMPOSITE ADSORBENTS  <b>(57) Abstract</b>  An adsorbent material comprises a composite of an inorganic gel such as silica gel and an organic polymer such as chitosan, the polymer being uniformly distributed throughout the gel. As part of the composite, a polymer placed in an environment in which it is normally soluble may be held in an insoluble state, and used for adsorption of pollutants from effluent or potable water.		

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## COMPOSITE ADSORBENTS

The present invention relates to compositions of matter for use as adsorbents or ion exchange materials.

Natural polymers such as chitosan, starch and alginic acid are useful adsorbents and ion exchangers in that they possess hydroxyl, amino or carboxyl groups which are all useful sites for adsorption or exchange. However the accessibility to these sites is generally poor because the compact structure of the polymer prevents diffusion of large ions. In addition they lack mechanical strength and appropriate form for use in industrial processes. Porous inorganic materials such as silica gel and silica alumina possess high surface areas and additionally have a form and mechanical strength appropriate to industrial use, but lack the adsorptive capacity of many polymers.

Organic polymers have been coated onto solid supports to improve their mechanical strength and accessible surface area. For example chitosan has been coated onto diatomaceous earth for effluent treatment processes.

However such coating processes do not make use of a large proportion of the available surface area of the porous support because the polymer solution, by virtue of viscosity, cannot penetrate the fine pores of the support.

The object of the present invention is to provide improved adsorbent materials which possess good mechanical strength, good accessibility to adsorption sites and high adsorptive capacity.

According to the present invention there is provided an adsorbent material comprising an inorganic gel and an organic polymer, wherein the polymer is uniformly and intimately distributed throughout the inorganic gel.

The present invention also provides a process for preparing a composition as defined in accordance with the invention, which process comprises forming an unstable inorganic sol which has dissolved therein an organic polymer, mixing vigorously and allowing or causing the unstable inorganic sol to gel entrapping the polymer therein.

Examples of inorganic gels for use in the present invention include silica gel, silica alumina gel or alumina gel. Formation of an unstable sol is conveniently accomplished by adding an acid such as sulphuric, nitric, hydrochloric, acetic or formic acid to a suitable precursor such as sodium silicate or in the case of silica alumina adding a solution of sodium aluminate to a solution of sodium silicate. Alternatively the unstable sol may be formed by taking a freshly prepared gel and by vigorous mechanical action reducing this to colloidal dimensions.

Examples of organic polymers for use with the invention include starch, dextran, chitosan, carboxymethyl cellulose, sodium carboxymethyl cellulose, polyvinyl alcohol, agar, agarose, carrageenan, gelatin, sodium alginate or albumin.

The organic polymer is added prior to the conversion of the inorganic sol into a gel, the addition being made at a point where the pH is appropriate to avoid precipitation of the polymer. Thus the polymer may be mixed with a precursor of the sol, such as sodium silicate or sodium aluminate, or with the sol itself. Organic polymers or salts of polymers which are soluble in alkaline solution such as starch or sodium alginate may be added conveniently to a precursor of the sol, whereas other polymers which are only soluble under neutral or acidic conditions are added to the unstable inorganic sol prior to gelation.

It is preferred that the composition contains between 5 and 50% by weight of the organic polymer.

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Preferably the composition is allowed to age for between 2 and 48 hours before being broken and washed. During this time the strength of the inorganic gel increases. The material may be used without drying but a stronger product is obtained if it is dried before use. Drying is conveniently undertaken by heating between 50 and 100°C for example at 80°C.

In a first embodiment of the invention a solution of sodium silicate is added to a solution of sulphuric acid such that the pH is in the range 5 to 7 after the addition. Before the sol thus formed gels, a solution of a polymer soluble under acidic conditions, such as a solution of chitosan in formic acid is added with vigorous stirring. The intimate mixture is then allowed to gel to a continuous mass. This is aged for a period of up to 48 hours after which it is broken through a sieve into water, washed and dried.

In a second embodiment of the invention a solution of a polymer soluble in alkali such as a solution of starch is added to a solution of sodium silicate and thoroughly mixed. A solution of sodium aluminate is then added with stirring and the intimate mixture is allowed to gel to a continuous mass. The gel is aged for up to 48 hours after which it is broken through a sieve, washed and dried.

The particle size of the material after drying may be conveniently controlled by selection of the dimensions of the sieve through which the wet gel is broken.

During the course of work on the present invention I have found that when the material of the invention is treated with a solution of ammonium hydroxide before or after drying the adsorption capacity towards metal ions in solution is considerably increased.

A particular benefit of the material according to the present invention is that a polymer which is normally soluble in water may be held in an insoluble state in an aqueous environment. Thus,

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for example, sodium carboxymethyl cellulose may be used for water treatment since when combined intimately with for example silica gel according to the present invention it is held within the rigid structure of the inorganic gel such that little leaching occurs with time. Where the material must be used in an aggressive environment, for example at elevated temperatures, the organic polymer may be cross-linked within the structure by for example treatment with a solution of formaldehyde or glutaraldehyde, though such treatment will reduce the adsorptive capacity.

Compositions according to the invention have application in liquid effluent treatment, for the removal of heavy metals and other toxic materials, in the treatment of potable water, in separation processes and ion exchange, and in biocatalyst and heterogeneous catalyst support.

The invention will be further apparent from the following examples :-

#### EXAMPLE 1

To a solution of formic acid (20 ml formic acid in 200 ml water) was added slowly with stirring, 200 ml of 50% commercial sodium silicate (29.9%  $\text{SiO}_2$ ). To this was added 100 ml of a solution of 4% chitosan in water containing 4 ml formic acid, the addition being completed within 3 minutes. The mixture was stirred vigorously for 2 minutes then allowed to stand while a gel formed. After 24 hours the gel was broken, washed and dried to yield 60 g of a composite which had a pore volume of 0.36 ml/ml, or 0.32 ml/g, a density of 1.14 g/cm<sup>3</sup>, a surface area of 150 m<sup>2</sup>/g, and a high adsorption capacity for dyes and organics such as phenol.

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## EXAMPLE 2

20 g of starch was dissolved in 200 ml of boiling water and the solution was cooled. This was added to a stirred solution of 36 ml of sodium silicate in 100 ml water. Stirring was continued while 3.9 ml conc. sulphuric acid in 100 ml water was added. After 1 minute stirring was discontinued and a gel formed which was aged for 24 hours before being broken, washed and dried. Microscopic examination of the material stained with iodine showed that the composite gel was homogeneous. The material actively removed metal ions such as copper and chromium from solution.

## EXAMPLE 3

10 g of starch was dissolved in 100 ml boiling water and the solution was cooled. This was added to a solution of 36 ml sodium silicate in 200 ml of water and the solution was stirred while 16.4 g of sodium aluminate in 200 ml water was added. Stirring was stopped to allow gelation and the cogel was aged for 12 hours. The gel was then broken, washed and dried. This composite could be used under more alkaline conditions than that of Example 2.

## EXAMPLE 4

80 ml of 50% sodium silicate was stirred while 1.6 ml conc. sulphuric acid in 100 ml water was added. To the stirred mixture, 40 ml of ovalbumin was added and stirring continued for 5 minutes. Gelation took several hours after which the gel was aged for a further 48 hours before being broken, washed and dried to produce an albumin/silica gel composite which actively adsorbed proteins.

## EXAMPLE 5

1.952 l of formic acid was added to 20.870 l of water. A second solution comprising 10.1 l of sodium silicate and 8.696 l of water was added to the first over a period of minutes with vigorous stirring. To this was added a solution containing 417.5 g chitosan

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in 11.305 l of water and 417.5 ml formic acid and vigorous stirring continued for 8 minutes. The mass gelled within 30 minutes and was aged for 48 hours after which it was broken through a 5 mm sieve into a 3% solution of ammonium hydroxide. The broken gel was allowed to stand in this solution for 24 hours before being washed and dried. After drying the material had a particle size of approximately 2 mm.

## EXAMPLE 6

A column 2.5 cm in diameter and 56 cm long was packed with the material of Example 5 and a solution containing 10 milligram/litre of lead was passed through the material at 15°C. The effluent from the column was analysed and found to contain less than 1 microgram/litre of lead. Similar results were obtained for aluminium.

## EXAMPLE 7

A sample of the material prepared in Example 5 was placed in a 1% solution of copper nitrate at 15°C. The solution was analysed before and after equilibrium adsorption. The adsorption capacity for copper was 160 mg Cu per g chitosan. Using an acidified solution of copper sulphate the adsorption capacity was similarly measured at 175 mg Cu per gram chitosan.

## EXAMPLE 8

A solution of 5 g sodium carboxymethyl cellulose in 100 ml water was added to a solution containing 100 ml sodium silicate and 84 ml water. This was added with vigorous stirring to 200 ml of 10% formic acid. After gelation the mass was allowed to age for 48 hours and then broken into 1.5 % ammonium hydroxide. After standing in this solution overnight it was washed and dried.



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## EXAMPLE 9

A sample of the material of Example 8 was placed in a 1% solution of copper sulphate and the solution analysed before and after equilibrium adsorption. The adsorption capacity for copper was found to be 187 mg/g polymer.

## CLAIMS

1. An adsorbent material comprising an inorganic gel and an organic polymer, wherein the polymer is uniformly and intimately distributed throughout the inorganic gel.
2. A material according to Claim 1 wherein the inorganic gel is of silica, silica alumina or alumina.
3. A material according to Claim 1 wherein the organic polymer is starch, dextran, chitosan, carboxymethyl cellulose, sodium carboxymethyl cellulose, polyvinyl alcohol, agar, agarose, carrageenan, gelatin, sodium alginate or albumin.
4. A material according to Claim 1 wherein the organic polymer comprises between 5 and 50% by weight of the material.
5. A process for preparing a material as claimed in any of the preceding claims which comprises forming an unstable inorganic sol which has dissolved therein an organic polymer, mixing vigorously and allowing or causing the unstable inorganic sol to gel entrapping the polymer therein.
6. A process according to Claim 5 wherein the organic polymer is added to a precursor of the inorganic sol.
7. A process according to Claim 5 wherein the organic polymer is added to the inorganic sol before gelation.
8. A process according to Claim 5 wherein the gel is subsequently allowed to age for between 2 and 48 hours.
9. A process according to Claim 5 wherein the gel is subsequently treated with ammonium hydroxide.
10. An adsorption process utilising an adsorbent material as hereinbefore described.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 89/00245

<b>I. CLASSIFICATION F SUBJECT MATTER</b> (if several classification symbols apply, indicate all) * According to International Patent Classification (IPC) or to both National Classification and IPC IPC <sup>4</sup> : B 01 J 20/28														
<b>II. FIELDS SEARCHED</b> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched <sup>7</sup></div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; border-bottom: 1px solid black;">Classification System</th> <th style="width: 75%; border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="border-right: 1px solid black; padding: 5px;">IPC<sup>4</sup></td> <td style="padding: 5px;">B 01 J</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *</div>			Classification System	Classification Symbols	IPC <sup>4</sup>	B 01 J								
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<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT *</b> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black;">Category *</th> <th style="width: 70%; border-bottom: 1px solid black;">Citation of Document, <sup>11</sup> with Indication, where appropriate, of the relevant passages <sup>12</sup></th> <th style="width: 20%; border-bottom: 1px solid black;">Relevant to Claim No. <sup>13</sup></th> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;">EP, A, 0180934 (DECHEMA) 14 May 1986, see pages 19,20 --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-8,10</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">GB, A, 1574414 (U.K.A.E.A.) 3 September 1980, see pages 9,10; claims --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1,2,3,10</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">EP, A, 0048110 (U.K.A.E.A.) 24 March 1982, see pages 1-3; claims ----</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1</td> </tr> </table>			Category *	Citation of Document, <sup>11</sup> with Indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>	X	EP, A, 0180934 (DECHEMA) 14 May 1986, see pages 19,20 --	1-8,10	A	GB, A, 1574414 (U.K.A.E.A.) 3 September 1980, see pages 9,10; claims --	1,2,3,10	A	EP, A, 0048110 (U.K.A.E.A.) 24 March 1982, see pages 1-3; claims ----	1
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"G" document member of the same patent family</p> </div> </div>														
<b>IV. CERTIFICATION</b> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;">           Date of the Actual Completion of the International Search   <div style="text-align: center;">1st June 1989</div> </td> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;">           Date of Mailing of this International Search Report   <div style="text-align: center;">20 JUN 1989</div> </td> </tr> <tr> <td style="border-bottom: 1px solid black; padding: 5px;">           International Searching Authority   <div style="text-align: center;">EUROPEAN PATENT OFFICE</div> </td> <td style="border-bottom: 1px solid black; padding: 5px;">           Signature of Authorized Officer  <div style="text-align: center;">   <b>P.C.G. VAN-DER PUTTEN</b> </div> </td> </tr> </table>			Date of the Actual Completion of the International Search  <div style="text-align: center;">1st June 1989</div>	Date of Mailing of this International Search Report  <div style="text-align: center;">20 JUN 1989</div>	International Searching Authority  <div style="text-align: center;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: center;">   <b>P.C.G. VAN-DER PUTTEN</b> </div>								
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# ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

GB 8900245

SA 27720

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0180934	14-05-86	DE-A- 3440444	07-05-86
GB-A- 157414		None	
EP-A- 0048110	24-03-82	JP-A- 57081830	22-05-82
		US-A- 4443339	17-04-84

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